



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number:

**0 653 392 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art.  
158(3) EPC

(21) Application number: 94915269.8

(51) Int. Cl.<sup>6</sup>: **C04B 38/00**

(22) Date of filing: 19.05.94

(96) International application number:  
**PCT/JP94/00803**

(87) International publication number:  
**WO 94/27929 (08.12.94 94/27)**

(30) Priority: 20.05.93 JP 118711/93

(43) Date of publication of application:  
17.05.95 Bulletin 95/20

(84) Designated Contracting States:  
**DE FR GB IT**

(71) Applicant: **SUMITOMO ELECTRIC INDUSTRIES, LTD**  
5-33, Kitahama 4-chome,  
Chuo-ku  
Osaka-shi,  
Osaka-fu 541 (JP)

(72) Inventor: **TAKEUCHI, Hisao, Itami Works of Sum. El.Ind, Ltd**  
1-1, Koyakita 1-chome  
Itami-shi  
Hyogo 664 (JP)  
Inventor: **NAKAHATA, Seiji Itami Works of Sum. El. Ind.,Ltd.**

1-1, Koyakita 1-chome  
Itami-shi  
Hyogo 664 (JP)  
Inventor: **MATSUURA, Takahiro Itami Works of Sum.El.Ind.,Ltd**  
1-1, Koyakita 1-chome  
Itami-shi  
Hyogo 664 (JP)  
Inventor: **KAWAI, Chihiro Itami Works of Sum.El. Ind.,Ltd**  
1-1, Koyakita 1-chome  
Itami-shi  
Hyogo 664 (JP)

(74) Representative: **Kirschner, Klaus Dieter, Dipl.-Phys. et al**  
Patentanwälte  
Herrmann-Trentepohl, Kirschner,  
Grosse, Bockhorni & Partner  
Forstenrieder Allee 59  
D-81476 München (DE)

(54) **POROUS CERAMIC AND PROCESS FOR PRODUCING THE SAME.**

(57) A porous ceramic combining a high porosity with a high strength and serving as a catalyst support or a filter for removing foreign matter from fluid. A porous ceramic having a porosity of 30 % or above comprises mainly columnar ceramic particles having an aspect ratio of 3 or above. In particular, a porous silicon nitride ceramic comprises mainly  $\text{Si}_3\text{N}_4$  wherein prismatic  $\beta\text{-Si}_3\text{N}_4$  particles amount to at least 60 % of the total amount of silicon nitride particles and further contains at least one compound of a rare earth element in an amount of 1-20 vol.% in terms of the oxide of the rare earth element. The silicon nitride ceramic may further contain at least one compound of a group IIa, group IIIb or transition metal element in an amount of at most 5 vol.% in terms of the oxide of the element. The porous silicon nitride ceramic is produced by heat-treating a molding of a powdery mixture comprising powdery silicon nitride and a powdery rare earth compound at 1,500 °C or above in a nitrogen-containing atmosphere.

**EP 0 653 392 A1**

## Technical Field

The present invention generally relates to a ceramics porous body which is useful as a filter material for removing foreign matters from a fluid or a catalytic carrier, and more specifically, it relates to a silicon nitride ceramics porous body and a method of preparing the same.

## Background Art

As porous bodies which are employed for filter materials or catalytic carriers, known are those consisting of various materials such as resin, metals or ceramics. Among these, a filter or a catalytic carrier consisting of a ceramics material is generally employed under environment of a high temperature or strong corrosiveness which cannot be coped by other materials. A filter or a catalytic carrier consisting of oxide ceramics such as alumina ( $\text{Al}_2\text{O}_3$ ) has already been put into practice.

As to a porous body consisting of nonoxide ceramics, on the other hand, only small examples have been put into practice while Japanese Patent Laying-Open No. 63-291982 discloses a silicon nitride based or silicon carbide based porous body which is prepared by a heat treatment. Further, Japanese Patent Laying-Open No. 1-188479 discloses a method of compacting mixed powder of silicon powder and silicon nitride powder of relatively coarse particles and thereafter nitriding the same thereby preparing a porous body as a solid target.

As hereinabove described, it is difficult to use a porous body consisting of resin or a metal under a high temperature or corrosive atmosphere. It is inevitably necessary to employ a porous body which is made of ceramics for a filter for removing foreign matters from a high-temperature exhaust gas or a carrier serving as a catalyst for decomposing a harmful matter.

As such porous bodies which are made of ceramics, those of alumina have been put into practice. While the porous bodies of alumina are varied in pore size, porosity and bending strength, that having porosity of 35 to 40 % and a mean pore size of 25 to 130  $\mu\text{m}$  has bending strength of 20 to 35 MPa, and strength of the porous body is insufficient depending on its use.

In the silicon nitride based porous body which is disclosed in the aforementioned Japanese Patent Laying-Open No. 63-291882, porosity is less than 30 % and fluid permeability is insufficient. In general, strength of ceramics tends to be reduced following increase in porosity, and it has been extremely difficult to attain compatibility between the porosity and the strength.

Accordingly, the present invention has been proposed in order to solve the aforementioned problems, and an object thereof is to provide a ceramics porous body having high porosity as well as high strength.

The inventors have made deep study on the aforementioned subject, and discovered that it is possible to prepare a silicon nitride ceramics porous body which is mainly composed of columnar  $\beta\text{-Si}_3\text{N}_4$  ( $\beta$ -silicon nitride) crystal grains and capable of maintaining high strength also when its porosity is high, by heat treating a compact of mixed powder of silicon nitride ( $\text{Si}_3\text{N}_4$ ) powder and prescribed additive powder at a high temperature.

Namely, a ceramic porous body according to the present invention is generally characterized in that a ceramics porous body having porosity of at least 30 % is mainly composed of columnar ceramics grains having an aspect ratio of at least 3. Specifically, it is a porous body having a mean pore size of at least 0.05  $\mu\text{m}$  and not more than 12  $\mu\text{m}$ . Further, the crystal grains preferably have forms of hexagonal poles.

More specifically, the ceramics porous body according to the present invention is a silicon nitride ceramics porous body which is mainly composed of silicon nitride with a ratio of at least 60 %, preferably at least 90 %, of  $\beta\text{-Si}_3\text{N}_4$  columnar grains with respect to the entire silicon nitride grains, contains at least one compound of a rare earth element by at least 1 volume % and not more than 20 volume % in terms of an oxide of the rare earth element, and has porosity of at least 30 %.

The aforementioned silicon nitride ceramics porous body may contain at least one of compounds of elements of the groups IIa and IIb of the periodic table and transition metal elements by not more than 5 volume % in terms of an oxide of each element. Further, the silicon nitride ceramics porous body according to the present invention preferably has bending strength of at least 80 MPa at an ordinary temperature, and bending strength of at least 50 MPa at a temperature of 1000 °C.

In summary, further, a method of preparing a silicon nitride ceramics porous body according to the present invention comprises the following steps:

- a. A step of adding at least one compound powder of a rare earth element by at least 1 volume % and not more than 20 volume % in terms of an oxide of the rare earth element, or further adding at least one of compounds of elements of the groups IIa and IIb of the periodic table and transition metal elements

by not more than 5 volume % in terms of an oxide of each element, to silicon nitride powder, thereby preparing mixed powder.

b. A step of preparing a compact from the aforementioned mixed powder.

c. A step of heat treating the compact in a nitrogen atmosphere at a temperature of at least 1500 °C and not more than 2100 °C.

In the present invention, the compound of a rare earth element acts to react with  $\text{SiO}_2$  existing on the surface of the raw material of the silicon nitride ( $\text{Si}_3\text{N}_4$ ) powder during the heat treatment for forming a liquid phase and solidly dissolving  $\text{Si}_3\text{N}_4$ , thereby precipitating columnar  $\beta\text{-Si}_3\text{N}_4$  crystal grains. Further, the compound of the rare earth element acts to exist outside the  $\beta\text{-Si}_3\text{N}_4$  grains as a grain boundary phase after the heat treatment, for joining  $\beta\text{-Si}_3\text{N}_4$  and maintaining strength. The rare earth element indicates an Sc, Y or lanthanoid elements. The additional ratio of the compound of the rare earth element is suitably in the range of 1 to 20 volume % in terms of an oxide, and more preferably 2 to 10 volume %. The form of the grain boundary phase is a silicate such as  $\text{Y}_2\text{O}_3 \cdot \text{SiO}_2$ , or an oxynitride such as  $\text{Y}_2\text{O}_3 \cdot \text{Si}_3\text{N}_4$ . Columnarization of the  $\beta\text{-Si}_3\text{N}_4$  crystal grains is not sufficient if the additional quantity of the compound of the rare earth element is less than 1 volume %, while oxidation resistance and strength at a high temperature are reduced if the amount exceeds 20 volume % and it leads to increase in preparation cost since the rare earth element is generally high-priced.

The compound(s) of the element(s) of the group(s) IIa and/or IIIb of the periodic table and/or the transition metal element(s) is added when a sintered body is prepared, in general. The aforementioned compound of the rare earth element acts to reduce a liquid phase forming temperature, facilitate densification and improve strength when the same is employed with the compound(s) of the element(s) of the group(s) IIa and/or IIIb of the periodic table and/or the transition metal element(s). The elements of the group IIa of the periodic table are Be, Mg, Ca, Sr and the like, the elements of the group IIIb are B, Al, Ga and the like, and the transition metal elements are Fe, Ti, Zr and the like.

In view of preparation of a porous body having high porosity, the additional ratio of the compound of such an element is preferably small. The additional amount is suitably not more than 5 volume % in terms of an oxide of each element, preferably not more than 2 volume %, and more preferably not more than 1 volume %.

Due to addition of the compound(s) of the element(s) of the group(s) IIa and/or IIIb of the periodic table and/or the transition metal element(s), on the other hand, the liquid phase is formed from a lower temperature region, whereby grain growth is also formed from a low temperature region. This is conceivably because the grain growth is caused by re-precipitation of  $\text{Si}_3\text{N}_4$  which is dissolved in the liquid phase, to reduce a grain growth starting temperature. When the compound(s) of the element(s) of the group(s) IIa and/or IIIb and/or the transition metal element(s) is added, therefore, it is possible to obtain a high-strength porous body at a low temperature, thereby attaining an advantage in view of the preparation cost. Further, such grain growth in a low temperature region tends to form fine crystal grains, whereby it is possible to prepare a porous body having a small pore size.

When the additional ratio of the compound(s) of the element(s) of the group(s) IIa and/or IIIb and/or the transition metal element(s) exceeds 5 volume %, densification is disadvantageously caused before columnar grain growth takes place to reduce porosity of the porous body while oxidation resistance is reduced due to a high densification effect from the low temperature region.

Particularly when a compound of a IVa group element such as Ti among transition metals is added, the compound reacts with  $\beta\text{-Si}_3\text{N}_4$  at a high temperature of at least 1600 °C and it is possible to increase bonding strength between the crystal grains, whereby a porous body of high strength can be obtained.

While the  $\text{Si}_3\text{N}_4$  powder employed as a raw material is mainly composed of  $\alpha\text{-Si}_3\text{N}_4$  in general,  $\beta\text{-Si}_3\text{N}_4$  or amorphous silicon nitride may alternatively be employed as the raw material. A mean grain size of the silicon nitride powder is preferably at least 0.1  $\mu\text{m}$  and not more than 20  $\mu\text{m}$ . If the mean grain size of the silicon nitride powder is less than 0.1  $\mu\text{m}$ , agglomeration of the powder materials is so intensely caused that density of the compact as obtained is not more than 30 % in relative density and handling strength of the compact as well as strength of the porous body after the heat treatment are insufficient. When the mean grain size of the silicon nitride powder exceeds 20  $\mu\text{m}$ , on the other hand, the degree of sintering by the heat treatment is reduced and the porous body cannot attain strength of at least 80 MPa.

It is most general to add the aforementioned compound of the rare earth element and the compound(s) of the element(s) of the group(s) IIa and/or IIIb of the periodic table and/or the transition metal element(s) as oxide powder materials, while it is also possible to add the same as compounds such as hydroxides or alkoxides which are decomposed to form powder materials of hydroxides or oxides. It is also possible to add these compounds in the form of nitride powder materials or the like.

These powder materials are mixed with each other by a prescribed method such as a ball mill method, and thereafter compacted. Also as to the compacting method, it is possible to employ a prescribed method such as die pressing or CIP (cold isostatic pressing). The compact density varies with the characteristics of the powder materials and target porosity of the porous body.

- 5 In order to facilitate growth of columnar grains as well as to attain high porosity, compact density is preferably low. In order to ensure strength which is required for handling the compact and to improve strength of the porous body after the heat treatment, however, it is necessary to prepare the compact with compact density exceeding a certain constant level. When commercially available  $\alpha$ - $\text{Si}_3\text{N}_4$  powder is employed, it is preferable to set the same at 30 to 60 % of theoretical density, more preferably at 35 to 50  
10 %. If only the compound of the rare earth element is added, porosity after the heat treatment exceeds 30 % when the compact density is less than 30 % in relative density, while the pore size is also increased and a porous body having high bending strength cannot be obtained even if columnar crystals are formed. When the compact density exceeds 60 % in relative density, on the other hand, it is possible to attain sufficiently high bending strength in the porous body, while porosity is less than 30 % and the pore size is also  
15 reduced.

- The compact as obtained is heat treated in a nitrogen atmosphere at a temperature of at least 1500 °C after a compacting assistant (resin or the like) is removed by thermal decomposition or the like. Transition to  $\beta$ - $\text{Si}_3\text{N}_4$  (in a case of employing  $\alpha$  powder) and grain growth (columnarization) proceed by the heat treatment, so that the compact is converted to a porous body mainly consisting of  $\beta$ - $\text{Si}_3\text{N}_4$  columnar grains.  
20 The heat treatment temperature varies with the composition of the additive, the grain size of the raw material powder, and the mean pore size and the porosity of the target porous body.

- When only a compound of a rare earth element such as  $\text{Y}_2\text{O}_3$  is added, for example, it is necessary to make the heat treatment in a high temperature region of at least 1700 °C. In this case, no remarkable densification proceeds even if the heat treatment is carried out at a higher temperature, and hence it is also  
25 possible to carry out the heat treatment in a temperature region extremely increasing the pore size. When the compound(s) of the element(s) of the group(s) IIa and/or IIIb of the periodic table and/or the transition metal element(s) is added in addition to the compound of the rare earth element, on the other hand, a liquid phase is formed from a low temperature region and  $\text{Si}_3\text{N}_4$  which is dissolved in this liquid phase is precipitated as columnar  $\beta$ -grains as described above, whereby it is possible to prepare a porous body of  
30 high strength also by a heat treatment in a low temperature region. However, a heat treatment which is carried out at a high temperature is improper as a method of preparing a porous body due to progress of densification. The densification is readily facilitated and the porosity is readily reduced as the additional amount of the compound(s) of the element(s) of the group(s) IIa and/or IIIb and/or the transition metal element(s) is increased.

- 35 As a heat treatment temperature for the compact, therefore, preferable is a temperature in the range of 1600 to 1900 °C if the amount of addition of the compound(s) of the element(s) of the group(s) IIa and/or IIIb and/or the transition metal element(s) is in excess of 0 volume % and not more than 1 volume %, 1600 to 1850 °C if the amount of addition of the compound is in excess of 1 volume % and not more than 2 volume %, and 1500 to 1700 °C if the amount of addition is in excess of 2 volume % and not more than 5  
40 volume %. In general, grain growth is not sufficient if the heat treatment temperature for the compact is less than 1500 °C.

- Since silicon nitride is increased in decomposition pressure at a high temperature, it is necessary to increase a nitrogen partial pressure by the heat treatment temperature. The atmosphere of the heat treatment may be an inert atmosphere containing nitrogen, and a mixed atmosphere of argon (Ar) or the like  
45 may be employed. While a temperature of at least 1700 °C is required when no compound(s) of the element(s) of the group(s) IIa and/or IIIb of the periodic table is added and a heat treatment at a temperature exceeding 2100 °C is advantageous for preparation of a porous body having a large pore size due to extreme grain growth, the nitrogen partial pressure must be at least several 100 atm. in order to control in the inventive range the porosity and the bending strength to at least 30 % and at least 80 MPa at  
50 the room temperature and at least 50 MPa at a temperature of 1000 °C respectively, and the cost is disadvantageously increased in view of the apparatus. When the heat treatment at a temperature exceeding 2100 °C is carried out, further, the use of the porous body is also disadvantageously restricted due to such a tendency that the bending strength of the porous body is also reduced. Thus, the heat treatment temperature is preferably not more than 2100 °C.

- 55 The porous body thus obtained has such a structure that  $\beta$ - $\text{Si}_3\text{N}_4$  columnar crystal grains are joined with each other by a grain boundary phase which is formed from the compound of the rare earth element, the compound(s) of the element(s) of the group(s) IIa and/or IIIb of the periodic table and/or the transition metal element(s), or an Si substance derived from the  $\text{Si}_3\text{N}_4$  powder, and exhibits high strength also when

porosity is high. It is conceivable that the reasons for such exhibition of the high strength are that the inventive porous body has such a structure that the columnar crystal grains are entangled with each other dissimilarly to a generally employed  $\text{Al}_2\text{O}_3$  porous body having a polycrystalline network structure consisting of spherical crystal grains, and that the columnar grains have extremely high strength (several GPa) since the same are single crystals having substantially no defects.

In this porous body, it is possible to arbitrarily control the mean pore size within the range of at least  $0.05\text{ }\mu\text{m}$  and not more than  $12\text{ }\mu\text{m}$  by the grain size of the raw material powder and the compact density. If the mean pore size is less than  $0.05\text{ }\mu\text{m}$ , development of the columnar grains is not sufficient and the aspect ratio thereof is less than 3. As the result, the porosity is disadvantageously reduced. When the mean pore size exceeds  $12\text{ }\mu\text{m}$ , on the other hand, the sizes of the crystal grains exceed  $36\text{ }\mu\text{m}$  in length and  $12\text{ }\mu\text{m}$  in breadth, to cause reduction in strength. Therefore, it is possible to employ the inventive porous body in the field of microfiltration etc. under a higher temperature or in a case of receiving a load, by controlling the mean pore size within the aforementioned range.

The ratio of  $\beta\text{-Si}_3\text{N}_4$  forming the columnar grains is preferably at least 60 % of the entire  $\text{Si}_3\text{N}_4$ , more preferably at least 90 %. The ratio of  $\beta\text{-Si}_3\text{N}_4$  is thus defined at an extremely high value, since  $\alpha\text{-Si}_3\text{N}_4$  which is another crystal form of  $\text{Si}_3\text{N}_4$  exhibits a spherical shape and causes reduction in strength. When  $\beta$ -silicon nitride columnar grains are at least 60 % and less than 90 % of the entire silicon nitride grains, the crystal structure thereof is in such a form that  $\alpha$ -silicon nitride columnar grains and  $\beta$ -silicon nitride columnar grains are composed with each other. In this case, the  $\beta$ -columnar grains couple portions where  $\alpha$ -crystal grains exist with each other, whereby it is possible to attain higher strength than that having a  $\beta$ -transition ratio of less than 60 %. Further, growth of such columnar grains also serves to prevent densification. Since  $\text{Si}_3\text{N}_4$  exhibits high oxidation resistance, the silicon nitride ceramics porous body can be employed with no breakage also when a high load is applied at a high temperature. Further, the silicon nitride ceramics porous body according to the present invention has high strength and a low coefficient of thermal expansion, whereby the same has excellent characteristics also as to a thermal shock.

While the silicon nitride ceramics porous body has been described, provision of both of high porosity and high strength essentially results from such a structure that the columnar grains are entangled with each other. Thus, another material having such a structure that columnar grains are entangled with each other also provides a similar effect. For example, such behavior is recognized also in aluminum nitride containing Si and a sintering assistant such as an oxide of a rare earth element as impurities. In general, therefore, it is possible to attain the aforementioned effect in a ceramics porous body having porosity of at least 30 % when the same is mainly composed of columnar ceramics grains having an aspect ratio of at least 3. The porous body is excellent in the aforementioned effect when the aspect ratio, which indicates a ratio of the length to the breadth of the columnar grains, is high in general, while an effect on improvement in strength is small if the same is less than 3.

Further, the columnar grains of the silicon nitride ceramics porous body are in hexagonal pole structures. In this case, the pores are formed by side surfaces of the hexagonal poles. It has been proved as the result of study by the inventors that, when the side surfaces which are planes are covered with a metal (platinum, for example) serving as a catalyst, the metal can uniformly adhere onto the surfaces to be improved in performance as a catalyst.

#### Best Mode for Carrying Out the Invention

##### Example 1

Yttrium oxide powder materials of  $0.5\text{ }\mu\text{m}$  in mean grain size (specific surface area:  $7\text{ m}^2/\text{g}$ ) were added to silicon nitride powder materials mainly composed of  $\alpha$ -silicon nitride ( $\alpha\text{-Si}_3\text{N}_4$ ) of  $0.3\text{ }\mu\text{m}$  in mean grain size (specific surface area:  $11\text{ m}^2/\text{g}$ ), and mixed with solvents of ethanol through a ball mill for 72 hours. Amounts of addition of the yttrium oxide powder materials are shown in Table 1.

Mixed powder materials obtained in the aforementioned manner were dried and thereafter compacted through a metal die of  $100\text{ mm} \times 100\text{ mm}$  under a pressure of  $20\text{ kg/cm}^2$  with addition of a compacting assistant. Compacts as obtained were about  $15\text{ mm}$  in thickness and about 35 % in relative density in every composition. The relative density was decided by dividing compact density which was calculated from measurement of the weight and dimensions by theoretical density, being a weighted mean of silicon nitride and the additive.

The compacts as obtained were heat treated under conditions shown in Table 1, thereby obtaining porous bodies. Test pieces of  $3\text{ mm} \times 4\text{ mm} \times 40\text{ mm}$  in size for a three-point bending test in accordance with JIS 1601 were cut out from the porous bodies. The test pieces were employed for measuring bending

strength values at an ordinary temperature and at 1000°C. Further, porosity values were calculated from the relative density values (porosity (%) = 100 - relative density (%)). In addition,  $\beta$ -transition ratios were obtained from X-ray diffraction peak intensity ratios, by carrying out X-ray diffraction through the porous bodies as obtained. The calculation expression is shown below.

$$(\beta\text{-transition ratio}) (\%) = \{A/(A + B)\} \times 100$$

where A represents X-ray diffraction peak intensity of  $\beta$ -silicon nitride, and B represents an X-ray diffraction peak intensity ratio of  $\alpha$ -silicon nitride.

A scanning electron microscope (SEM) was employed to observe broken-out sections, thereby obtaining mean crystal grain sizes. Mean pore sizes were measured with a mercury porosimeter. These measurement results are shown in Table 1.

Table 1

No.	Additive Y <sub>2</sub> O <sub>3</sub> (Vol%)	Heat Treatment Condition			Porous Body Characteristics						
		Temperature (°C)	Retention Time (H)	Pressure of Atmosphere (atm)	Porosity (%)	Mean Pore Size (μm)	Crystal Grain Size		Bending Strength		β-Transition Ratio (%)
							Length (μm)	Breadth (μm)	Ordinary Temperature (MPa)	100°C (MPa)	
1	0	1800	2	4	60	0.5	—	0.5	7	1	50
2	0.5	1800	2	4	45	0.8	1	0.5	80	80	100
3	1	1800	2	4	39	1.5	3	0.8	150	150	100
4	2	1800	2	4	48	1.8	12	0.8	130	100	100
5	4	1800	2	4	48	0.8	15	1.0	120	100	100
6	8	1800	2	4	58	3.5	20	1.5	100	85	100
7	12	1800	2	4	57	3.0	20	1.6	110	70	100
8	20	1800	2	4	55	4.0	18	1.8	100	60	100
9	30	1800	2	4	50	3.0	25	2.0	90	40	100
10	4	1500	2	4	61	0.3	—	0.4	5	0.7	5
11	4	1600	2	4	60	0.4	1.5	0.4	6	0.8	50
12	4	1700	2	4	58	1.0	3	0.5	85	55	50
13	4	1700	2	4	56	2.0	10	0.8	100	80	50
14	4	1800	2	4	55	2.5	15	1.2	120	100	100
15	4	1900	2	10	55	3.5	20	1.5	110	100	100
16	4	2000	2	40	54	8.0	35	2.0	90	80	100
17	4	2100	2	100	54	12.0	50	3.0	80	60	100
18	4	1800	1	4	54	2.5	12	1.2	120	90	100
19	4	1800	5	4	55	3.5	20	1.5	110	90	100
20	4	1800	2	10	57	3.0	20	1.5	110	100	100
21	4	1650	2	4	53	0.8	2.0	0.6	61	38	50
22	4	1700	2	4	52	1.0	2.3	0.7	80	50	60
23	4	2100	10	100	25	13.0	42	3.8	40	32	100
24	2	1700	20	10	28	0.04	0.11	0.04	65	28	75

## Example 2

Porous bodies were prepared by a method similar to that in Example 1 except that oxide powder materials of respective rare earth elements shown in Table 2 were employed as compounds of rare earth

elements in place of yttrium oxide powder materials, and valuated. The results are shown in Table 2. It is understood from the results that similar silicon nitride porous bodies are obtained also when rare earth oxides other than yttrium oxide are employed.

Table 2

Additive		Heat Treatment Condition			Porous Body Characteristics					
A Group Additive	Additional Ratio	Temperature (°C)	Retention Time (H)	Pressure of Atmosphere (atm)	Porosity (%)	Pore Size (μm)	Crystal Grain Size		Bending Strength	
	(Vol%)	(°C)	(H)	(atm)	(%)	(μm)	Length (μm)	Breadth (μm)	Ordinary Temperature (MPa)	1000°C (MPa)
										β-Transition Ratio (%)
$\text{La}_2\text{O}_3$	4	1800	2	4	50	2.0	18	1.4	130	100
$\text{CeO}_2$	4	1800	2	4	52	2.2	20	1.4	100	80
$\text{Nd}_2\text{O}_3$	4	1800	2	4	48	2.2	15	1.4	130	90
$\text{Gd}_2\text{O}_3$	4	1800	2	4	52	2.4	15	1.1	120	80
$\text{Dy}_2\text{O}_3$	4	1800	2	4	53	2.5	16	1.3	110	90
$\text{Yb}_2\text{O}_3$	4	1800	2	4	55	2.8	20	1.5	100	80
$\text{Y}_2\text{O}_3$	4	1800	2	4	55	2.5	15	1.2	120	100



Example 3

Porous bodies were prepared by a method similar to that in Example 1 except that yttrium oxide, being an oxide of a rare earth element, was added as an A group additive, and aluminum oxide, magnesium oxide and titanium oxide, being compounds of elements of the groups IIa and IIb of the periodic table and a transition metal element, were added as B group additional compounds, and evaluated. The results are shown in Table 3.

As obvious from Table 3, it is understood possible to prepare silicon nitride porous bodies at lower temperatures than Examples in which only rare earth oxides were added.

Table 3.1

No.	Additive				Heat Treatment Condition			Porous Body Characteristics						
	A Group Additive	Additional Ratio	B Group Additive	Additional Ratio	Temperature	Retention Time	Pressure of Atmosphere	Porosity	Pore Size	Crystal Grain Size		Bending Strength		β-Transition Ratio
										Length	Breadth	Ordinary Temperature	10 10°C	
1	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	0	1800	2	4	55	2.5	15	1.2	120	100	100
2	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	0.5	1800	2	4	45	2	15	1.5	150	100	100
3	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	1.2	1800	2	4	28	1.9	15	1.5	170	120	100
4	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	2	1800	2	4	12	1.5	15	1.5	220	150	100
5	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	5	1800	2	4	2	1	12	1.5	540	150	100
6	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	10	1800	2	4	4	1	10	2	350	210	100
7	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	0.5	1500	2	1	58	0.5	1.5	0.5	50	40	40
8	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	0.5	1600	2	1	54	1.5	7	0.7	80	40	90
9	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	0.5	1700	2	4	48	1.8	12	1	120	100	100
10	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	0.5	1750	2	4	44	2.2	15	1.2	130	100	100
11	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	0.5	1900	2	10	40	2.5	20	2.2	130	110	100
12	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	2	1700	2	4	35	1	10	1.2	110	80	100

Table 3.2

No.	Additive				Heat Treatment Condition			Porous Body Characteristics						
	A Group Additive	Additional Ratio	B Group Additive	Additional Ratio	Temperature (°C)	Retention Time	Pressure of Atmosphere	Porosity (%)	Pore Size (μm)	Crystal Grain Size		Bending Strength		β-Transition Ratio
										Length (μm)	Breadth (μm)	Ordinary Temperature (MPa)	1100°C (MPa)	
13	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	2	1750	2	4	31	1.3	15	1.3	140	80	100
14	Y <sub>2</sub> O <sub>3</sub>	4	Al <sub>2</sub> O <sub>3</sub>	5	1700	2	4	20	0.8	10	1.2	160	120	100
15	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	1500	2	4	53	0.9	2	0.5	70	50	70
16	Y <sub>2</sub> O <sub>3</sub>	4	MgO	1.2	1500	2	4	50	1	2.5	0.6	90	60	80
17	Y <sub>2</sub> O <sub>3</sub>	4	MgO	2	1500	2	4	42	1	3	0.7	100	60	90
18	Y <sub>2</sub> O <sub>3</sub>	4	MgO	5	1500	2	4	32	0.9	3	0.6	100	50	95
19	Y <sub>2</sub> O <sub>3</sub>	4	MgO	10	1500	2	4	26	0.8	4	0.8	130	40	100
20	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	1600	2	4	50	1.2	10	1.2	100	60	90
21	Y <sub>2</sub> O <sub>3</sub>	4	MgO	1.2	1600	2	4	42	1.2	10	1	110	70	95
22	Y <sub>2</sub> O <sub>3</sub>	4	MgO	2	1600	2	4	38	1.2	12	1	120	70	100
23	Y <sub>2</sub> O <sub>3</sub>	4	MgO	5	1600	2	4	30	1	12	1.3	150	70	100
24	Y <sub>2</sub> O <sub>3</sub>	4	MgO	10	1600	2	4	15	0.9	15	1.5	200	50	100

Table 3.3

No.	Additive				Heat Treatment Condition			Porous Body Characteristics						
	A Group Additive	Additional Ratio	B Group Additive	Additional Ratio	Temperature (°C)	Retention Time (H)	Pressure of Atmosphere (atm)	Porosity (%)	Pore Size (μm)	Crystal Grain Size		Bending Strength		β-Transition Ratio
										Length (μm)	Breadth (μm)	Ordinary Temperature (MPa)	1000°C (MPa)	
25	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	1800	2	4	42	1.8	20	1.8	140	100	100
26	Y <sub>2</sub> O <sub>3</sub>	4	MgO	1.2	1800	2	4	20	1.2	22	2	210	150	100
27	Y <sub>2</sub> O <sub>3</sub>	4	MgO	2	1800	2	4	2	—	25	2	500	300	100
28	Y <sub>2</sub> O <sub>3</sub>	4	MgO	5	1800	2	4	1	—	25	2.5	550	300	100
29	Y <sub>2</sub> O <sub>3</sub>	4	MgO	10	1800	2	4	1	—	20	2.5	450	270	100
30	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	1400	2	4	55	0.8	1	0.5	40	30	30
31	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	1700	2	4	45	1.5	15	1.6	130	90	100
32	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	1800	2	4	42	1.8	20	1.8	140	100	100
33	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	1900	2	10	35	2.3	25	2	120	80	100
34	Y <sub>2</sub> O <sub>3</sub>	4	MgO	0.5	2000	2	100	35	3	30	2.5	70	40	100
35	Y <sub>2</sub> O <sub>3</sub>	4	TiO <sub>2</sub>	0.5	1800	2	4	45	0.6	12	1.0	150	120	100
36	Y <sub>2</sub> O <sub>3</sub>	4	TiO <sub>2</sub>	1.2	1800	2	4	42	0.6	10	0.7	200	150	100

Table 3.4

No.	Additive				Heat Treatment Condition			Porous Body Characteristics						
	A Group Additive	Additional Ratio	B Group Additive	Additional Ratio	Temperature	Retention Time	Pressure of Atmosphere	Porosity	Pore Size	Crystal Grain Size		Bending Strength		β-Transition Ratio
										Length	Breadth	Ordinary Temperature	1000°C	
		(Vol%)		(Vol%)	(°C)	(H)	(atm)	(%)	(μm)	(μm)	(μm)	(MPa)	(MPa)	(%)
37	Y <sub>2</sub> O <sub>3</sub>	4	TiO <sub>2</sub>	2	1800	2	4	40	0.5	8	0.5	225	170	100
38	Y <sub>2</sub> O <sub>3</sub>	4	TiO <sub>2</sub>	5	1800	2	4	35	0.5	8	0.5	315	180	100
39	Y <sub>2</sub> O <sub>3</sub>	4	TiO <sub>2</sub>	10	1800	2	4	28	0.2	4	0.3	421	350	100
40	Y <sub>2</sub> O <sub>3</sub>	4	TiO <sub>2</sub>	0.5	1600	2	4	52	0.3	7	0.5	72	38	90
41	Y <sub>2</sub> O <sub>3</sub>	4	TiO <sub>2</sub>	0.5	1700	2	4	50	0.7	8	0.8	180	110	100
42	Y <sub>2</sub> O <sub>3</sub>	8	Al <sub>2</sub> O <sub>3</sub>	3.5	1650	10	10	18	0.03	0.09	0.04	79	42	72
43	Y <sub>2</sub> O <sub>3</sub>	8	Al <sub>2</sub> O <sub>3</sub>	0.5	2100	20	100	25	12.5	45	13	62	48	100
44	Y <sub>2</sub> O <sub>3</sub>	8	MgO	4.5	1600	10	10	10	0.01	0.02	0.01	66	18	68
45	Y <sub>2</sub> O <sub>3</sub>	8	MgO	0.2	2100	15	100	27	15.0	38	5	55	35	100
46	Y <sub>2</sub> O <sub>3</sub>	8	TiO <sub>2</sub>	4.5	1700	10	10	5	0.04	0.08	0.03	85	41	75
47	Y <sub>2</sub> O <sub>3</sub>	8	TiO <sub>2</sub>	0.8	2100	20	100	28	12.8	29	8	72	40	100

## Example 4

Silicon oxide powder (20.6 volume %) and yttrium oxide powder (1.2 volume %) of 0.5 μm in mean grain size were added to aluminum nitride powder of 0.5 μm in mean grain size, and mixed with a solvent

of ethanol in a ball mill for 72 hours.

Mixed powder thus obtained was dried and thereafter compacted through a metal die of 10 mm x 10 mm under a pressure of 20 kg/cm<sup>2</sup> with addition of a compacting assistant. Density of the compact as obtained was 37 % in relative density.

5 This compact was heat treated in the atmosphere at a temperature of 600 °C for 1 hour for removing the compacting assistant, and thereafter heat treated in nitrogen of the atmospheric pressure at a temperature of 1700 °C for 1 hour, to obtain a porous body. Porosity, a mean pore size and a mean aspect ratio of crystal grains of this porous body were 35 %, 1.6 μm and 4 respectively. Three-point bending strength values at an ordinary temperature and at 1000 °C were 90 MPa and 60 MPa respectively.

10

#### Example 5

α-silicon nitride raw powder materials of 0.3 μm, 7.0 μm and 12.0 μm in mean grain size were employed to prepare mixed powder materials so that yttrium oxide powder contents were 4 volume % in the case of the powder of 0.3 μm and 5 volume % in the cases of 7.0 μm and 12.0 μm by a method similar to that in Example 1, thereby preparing compacts having relative density values shown in Table 4. Compact density values were adjusted by changing uniaxial compacting pressures in the range of at least 1 kg/cm<sup>2</sup> and not more than 2000 kg/cm<sup>2</sup>. The compacts as obtained were treated and evaluated under the same conditions as those in Example 1 except that heat treatments after decomposition of a compacting assistant were carried out under the same conditions in nitrogen of 4 atm. at a temperature of 1800 °C for 2 hours. The evaluation results are shown in Table 4.

From these results, it is understood possible to control the mean pore sizes of the porous bodies obtained after the heat treatments by controlling the mean grain sizes of the raw powder materials and the density values of the compacts.

25

30

35

40

45

50

55

Table 4.1

Raw Material			Additive	Compact	Heat Treatment Condition			Characteristics						
Grain Size					Temperature	Retention Time	Pressure of Atmosphere	Porosity	Mean Pore Size	Crystal Grain Size		Bending Strength		$\mu$ -Transition Ratio
			Y <sub>2</sub> O <sub>3</sub>	Relative Density						Major Axis	Minor Axis	Ordinary Temperature	1000°C	
( $\mu\text{m}$ )		(Vol.%)	(%)	(%)	(°C)	(H)	(atm)	(%)	( $\mu\text{m}$ )	( $\mu\text{m}$ )	( $\mu\text{m}$ )	(MPa)	(MPa)	(%)
0.3		4	20		1800	2	4	72	1.6	22	1.7	40	35	100
0.3		4	25		1800	2	4	70	1.6	20	1.7	60	50	100
0.3		4	27		1800	2	4	67	1.5	20	1.5	70	50	100
0.3		4	30		1800	2	4	60	1.2	18	1.2	100	80	100
0.3		4	35		1800	2	4	48	0.8	15	1.0	120	100	100
0.3		4	40		1800	2	4	42	0.6	10	0.8	150	130	100
0.3		4	45		1800	2	4	40	0.5	6	0.5	180	150	100
0.3		4	50		1800	2	4	38	0.2	4	0.2	210	180	100
0.3		4	55		1800	2	4	35	0.1	2	0.1	280	230	100
0.3		4	60		1800	2	4	31	0.05	1	0.07	350	280	100
0.3		4	65		1800	2	4	27	0.03	1	0.06	400	350	100
0.3		4	70		1800	2	4	20	0.02	1	0.05	450	400	100
7.0		5	20		1800	2	4	50	5.1	22	2.5	50	40	100
7.0		5	28		1800	2	4	47	3.8	20	2.1	60	50	100

Table 4.2

Raw Material			Additive			Compact			Heat Treatment Condition			Characteristics						
Grain Size			Y <sub>2</sub> O <sub>3</sub>			Relative Density			Temperature	Retention Time	Pressure of Atmosphere	Porosity	Mean Pore Size	Crystal Grain Size		Bending Strength		11-Transition Ratio
														Major Axis	Minor Axis	Ordinary Temperature	1000°C	
(μm)	(Vol.%)	(%)	(°C)	(H)	(atm)	(%)	(μm)	(%)	(μm)	(μm)	(MPa)	(MPa)	(%)					
7.0	5	30	1800	2	4	43	2.4	18	1.7	88	70	100						
7.0	5	40	1800	2	4	40	1.8	15	1.2	130	100	100						
7.0	5	50	1800	2	4	38	1.2	14	1.1	210	150	100						
7.0	5	60	1800	2	4	32	0.7	12	0.8	220	180	100						
7.0	5	65	1800	2	4	19	0.3	10	0.5	250	200	100						
12.0	5	20	1800	2	4	60	6	28	3.0	50	30	100						
12.0	5	28	1800	2	4	60	4	25	2.5	82	65	100						
12.0	5	30	1800	2	4	58	3.5	16	1.8	105	88	100						
12.0	5	40	1800	2	4	53	3.1	12	1.7	170	103	100						
12.0	5	50	1800	2	4	50	2.0	8	1.4	190	120	100						
12.0	5	60	1800	2	4	37	1.5	7	1.3	210	180	100						
12.0	5	65	1800	2	4	28	1.2	5	1.1	240	200	100						
12.0	5	20	2100	2	100	25	13.2	45	11	43	18	100						

## Example 6

Silicon nitride ceramics porous bodies of 0.1 to 5.0 μm in mean pore size which were prepared by the inventive preparation method were worked into the form of discs of φ25 mm x 0.5 mm. These porous



bodies were employed to carry out permeation experiments through isopropyl alcohol (20 °C) and pure water (20 °C). The results are shown in Table 5. Table 5 shows flow rate results in a case of employing  $\alpha$ -alumina ceramics porous bodies having the same pore sizes as comparative examples.

It is understood from the results that liquid permeation flow rates of the silicon nitride porous bodies have higher performance than the alumina porous bodies.

Table 5

Material	Grain Size ( $\mu\text{m}$ )	Porosity (%)	IPA Flow Rate (ml/min/cm <sup>2</sup> )	Pure Water Flow Rate (ml/min/cm <sup>2</sup> )
Silicon Nitride	0.1	45	0.82	1.97
Silicon Nitride	0.2	48	2.01	4.82
Silicon Nitride	0.5	60	4.11	9.86
Silicon Nitride	1.0	60	14.1	33.8
Silicon Nitride	2.0	55	22.5	54.0
Silicon Nitride	5.0	50	40.3	96.7
$\alpha$ -Alumina	0.1	40	0.43	1.02
$\alpha$ -Alumina	0.2	40	1.06	2.55
$\alpha$ -Alumina	0.5	40	1.78	4.25
$\alpha$ -Alumina	1.0	40	4.96	11.9
$\alpha$ -Alumina	2.0	40	8.85	21.25
$\alpha$ -Alumina	5.0	40	17.7	42.5
IPA (isopropyl alcohol) flow rates and pure water flow rates are permeation flow rates in pressurization at 20 °C and 1.0 kg/cm <sup>2</sup> .				

#### Industrial Applicability

According to the present invention, as hereinabove described, it is possible to obtain a ceramics porous body having high porosity and high strength. This porous body, which is excellent in high temperature characteristics and chemical resistance, is useful as a filter which is employed at a high temperature or a catalytic carrier which is employed in an atmosphere having high corrosiveness.

#### Claims

- (amended) A ceramics porous body comprising porosity of at least 30 % and a mean pore size of at least 0.05  $\mu\text{m}$  and not more than 12  $\mu\text{m}$ , said ceramics porous body being mainly composed of ceramics crystal grains having forms of hexagonal poles with an aspect ratio of at least 3.
- (deleted)
- (deleted)
- A silicon nitride ceramics porous body comprising a ratio of at least 60 % of  $\beta$ -silicon nitride hexagonal pole shaped grains to entire silicon nitride grains and including at least one compound of a rare earth element by at least 1 volume % and not more than 20 volume % in terms of an oxide of said rare earth element, with porosity of at least 30 %.
- The silicon nitride ceramics porous body in accordance with claim 4, including at least one of compounds of elements of the groups IIa and IIIb of the periodic table and transition metal elements by not more than 5 volume % in terms of an oxide of each said element.

6. The silicon nitride ceramics porous body in accordance with claim 4, wherein bending strength at an ordinary temperature is at least 80 MPa.
7. The silicon nitride ceramics porous body in accordance with claim 4, wherein bending strength at a temperature of 1000 °C is at least 50 MPa.
8. A silicon nitride ceramics porous body comprising a ratio of at least 90 % of  $\beta$ -silicon nitride hexagonal pole shaped grains to entire silicon nitride grains and including at least one compound of a rare earth element by at least 1 volume % and not more than 20 volume % in terms of an oxide, with porosity of at least 30 %.
9. A method of preparing a silicon nitride ceramics porous body comprising a ratio of at least 60 % of  $\beta$ -silicon nitride hexagonal pole shaped grains to entire silicon nitride grains with porosity of at least 30 %, said method of preparing the silicon nitride ceramics porous body comprising the steps of:
  - adding at least one compound powder of a rare earth element to silicon nitride powder by at least 1 volume % and not more than 20 volume % in terms of an oxide of said rare earth element, thereby preparing mixed powder;
  - preparing a compact from said mixed powder; and
  - heat treating said compact in a nitrogen atmosphere at a temperature of at least 1700 °C and not more than 2100 °C.
10. The method of preparing a silicon nitride ceramics porous body in accordance with claim 9, wherein said silicon nitride powder comprising a mean grain size in the range of at least 0.1  $\mu\text{m}$  and not more than 20  $\mu\text{m}$  is employed and density of said compact as obtained is controlled in the range of at least 30 % and not more than 60 % in relative density in said step of preparing said compact from said mixed powder.
11. A method of preparing a silicon nitride ceramics porous body comprising a ratio of at least 60 % of  $\beta$ -silicon nitride hexagonal pole shaped grains to entire silicon nitride grains with porosity of at least 30 %, said method of preparing the silicon nitride ceramics porous body comprising the steps of:
  - adding at least one compound powder of a rare earth element by at least 1 volume % and not more than 20 volume % in terms of an oxide of said rare earth element and at least one of compounds of elements of the groups IIa and IIb of the periodic table and transition metal elements by an amount exceeding 0 volume % and not more than 1 volume % in terms of an oxide of said element to silicon nitride powder, thereby preparing mixed powder;
  - preparing a compact from said mixed powder; and
  - heat treating said compact in a nitrogen atmosphere at a temperature of at least 1600 °C and not more than 1900 °C.
12. A method of preparing a silicon nitride ceramics porous body comprising a ratio of at least 60 % of  $\beta$ -silicon nitride hexagonal pole shaped grains to entire silicon nitride grains with porosity of at least 30 %, said method of preparing the silicon nitride ceramics porous body comprising the steps of:
  - adding at least one compound powder of a rare earth element by at least 1 volume % and not more than 20 volume % in terms of an oxide of said rare earth element and at least one of compounds of elements of the groups IIa and IIb of the periodic table and transition metal elements by at least 1 volume % and not more than 2 volume % in terms of an oxide of said element to silicon nitride powder, thereby preparing mixed powder;
  - preparing a compact from said mixed powder; and
  - heat treating said compact in a nitrogen atmosphere at a temperature of at least 1600 °C and not more than 1850 °C.
13. A method of preparing a silicon nitride ceramics porous body comprising a ratio of at least 60 % of  $\beta$ -silicon nitride hexagonal pole shaped grains to entire silicon nitride grains with porosity of at least 30 %, said method of preparing the silicon nitride ceramics porous body comprising the steps of:
  - adding at least one compound powder of a rare earth element by at least 1 volume % and not more than 20 volume % in terms of an oxide of said rare earth element and at least one of compounds of elements of the groups IIa and IIb of the periodic table and transition metal elements by an amount exceeding 2 volume % and not more than 5 volume % in terms of an oxide of said element to silicon

nitride powder, thereby preparing mixed powder;  
preparing a compact from said mixed powder; and  
heat treating said compact in a nitrogen atmosphere at a temperature of at least 1500 °C and not  
more than 1700 °C.

5

10

15

20

25

30

35

40

45

50

55

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/JP94/00803

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
Int. Cl <sup>5</sup> C04B38/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
Int. Cl <sup>5</sup> C04B38/00-3/10, C04B35/00-35/84		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1994 Kokai Jitsuyo Shinan Koho 1971 - 1994		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A2, 2-089812 (Ibiden Co., Ltd.), March 29, 1990 (29. 03. 90), (Family: none)	1-13
Y	JP, A2, 3-281740 (NGK Insulators, Ltd.), December 12, 1991 (12. 12. 91), (Family: none)	1-13
Y	JP, A2, 4-37668 (Tonen Corp.), February 7, 1992 (07. 02. 92), (Family: none)	1-13
Y	JP, A2, 62-18621 (Etsuro Kato), August 15, 1987 (15. 08. 87), (Family: none)	1-13
Y	JP, 4-285079 (Ibiden Co., Ltd.), October 9, 1992 (09. 10. 92), (Family: none)	1-13
Y	JP, A2, 61-53176 (Nippondenso Co., Ltd.), March 17, 1986 (17. 03. 86), (Family: none)	1-13
Y	JP, A2, 63-156070 (Kyocera Corp.), June 29, 1988 (29. 06. 88), (Family: none)	1-13
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another claim or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>		
Date of the actual completion of the international search July 1, 1994 (01. 07. 94)		Date of mailing of the international search report July 26, 1994 (26. 07. 94)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP94/00803

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP, A2, 3-170376 (Kyocera Corp.), July 23, 1991 (23. 07. 91), (Family: none)	1-13
Y	JP, A2, 4-219374 (Kyocera Corp.), August 10, 1992 (10. 08. 92), (Family: none)	1-13
Y	JP, A2, 56-75546 (Toshiba Corp.), June 22, 1981 (22. 06. 81) & US, A, 4332909	1-13
Y	JP, A2, 59-199584 (Toshiba Tungaloy Co., Ltd.), November 12, 1984 (12. 11. 84) & EP, A2, 123292 & DE, C, 3483588	1-13
Y	JP, A2, 4-357170 (Sumitomo Electric Industries, December 10, 1992 (10. 12. 92), (Family: none)	1-13
Y	JP, A2, 1-93469 (Toyota Central Research and Development Laboratories, Inc.), April 12, 1989 (12. 04. 89), (Family: none)	1-13